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European Patent Office
Office européen des brevets



(11) Publication number:

0 265 983 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **22.05.91** (51) Int. Cl.⁵: **C03C 4/12, C03C 3/095, H01J 29/20**
- (21) Application number: **87201900.5**
- (22) Date of filing: **05.10.87**

(54) Luminescent quartz glass, method of preparing such a glass and luminescent screen provided with such a glass.

(30) Priority: **08.10.86 NL 8602519**

(43) Date of publication of application:
04.05.88 Bulletin 88/18

(45) Publication of the grant of the patent:
22.05.91 Bulletin 91/21

(94) Designated Contracting States:
BE DE FR GB NL

(56) References cited:
EP-A- 0 199 409
US-A- 3 927 224

JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 52, no. 6, 21st June 1969, page 344, Columbus, Ohio, US; R. ROY: "Gel route to homogeneous glass preparation"

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Description

The invention relates to a luminescent quartz glass activated by a rare earth metal and comprising as a glass matrix oxide mainly SiO_2 and furthermore 0 to 0.15 mol of MO, per mol of SiO_2 , in which MO represents at least one of the oxides Al_2O_3 , B_2O_3 , P_2O_5 , ZrO_2 , Sc_2O_3 , Y_2O_3 , La_2O_3 , Gd_2O_3 , Lu_2O_3 , ZnO , the alkali metal oxides and the alkaline earth metal oxides. The invention also relates to a method of preparing such a luminescent quartz glass and to a luminescent screen provided with such a luminescent quartz glass.

Luminescent quartz glasses have been known for a comparatively long time. United States Patents 3,527, 711, 3,634,711, 3,855,144 and 3,935,119, for example, describe such glasses whose SiO_2 content is very high (generally at least 99% by weight) and in which preferably rare earth metals are used as activators. These rare earth metal activators are used in very low concentrations with a maximum concentration of 5000 ppm (rare earth metal atoms relative to Si atoms) being stated. Also if a plurality of rare earth metals is used as an activator the concentration of all activators combined is not to exceed this maximum value and preferably even the limit of 2000 ppm is not exceeded. Expressed in mol.% of the (trivalent) rare earth metal oxide relative to SiO_2 the said limits of 5000 and 2000 ppm are 0.25 and 0.1 mol%, respectively. In the above cited patents it is stated that less transparent products are obtained when the given maximum values of the activator concentration are exceeded. Less transparent and coloured luminescent materials have the drawback of a too low luminous flux so that they are not usable in practice.

United States Patent 3,459,673 describes a method of preparing a quartz glass activated by rare earth metals in which the starting material is a hydrolysable silicon compound and an aqueous solution of a salt of a rare earth metal soluble in water. Also in this publication very low activator concentrations are stated (in the examples concentrations of the order of several hundred ppm).

A luminescent quartz glass of the type described in the opening paragraph is known from Netherlands Patent Application 6605957. In this application a terbium-activated glass is described whose glass matrix, that is to say, the glass composition without an activator oxide, mainly consists of SiO_2 but also comprises up to approximately 0.20 mol per mol of SiO_2 of other oxides mentioned by name. According to this patent application the addition of these other oxides renders a higher terbium concentration possible. The maximum concentration is, however, only 0.5 mol% of Tb_2O_3 per mol of SiO_2 , that is to say, only a factor of 2 higher than the maximum concentration in the aforementioned United States patents.

A great drawback of the known luminescent quartz glasses is that they have a low efficiency compared with crystalline luminescent materials. Particularly the quantum efficiency upon excitation by ultraviolet radiation is often found to be a factor of 5 to 10 smaller than the quantum efficiencies which can be achieved with efficient crystalline materials.

The object of the invention is to provide luminescent quartz glasses having high conversion efficiencies and notably high quantum efficiencies upon excitation by ultraviolet radiation.

According to the invention a luminescent quartz glass of the type described in the opening paragraph is therefore characterized in that the glass comprises at least one of the oxides Tb_2O_3 and Ce_2O_3 as activator oxides in a quantity of 0.75 to 15 mol% calculated with respect to the glass matrix oxides.

The invention is based on the recognition that the rare earth metals Tb and Ce, when used as activators in quartz glasses, have an optimum effect if they are used in a concentration range which is much higher than the range hitherto assumed to be optimum. The activator concentration in the quartz glasses according to the invention is chosen of the same order as the concentration in crystalline luminescent materials and it has been found that upon excitation by ultraviolet radiation efficiencies can be achieved which are comparable with those of the crystalline materials. A condition is that the glass matrix is transparent to the exciting ultraviolet radiation because otherwise excitation energy is lost due to absorption in the matrix itself, and that the glass is free from impurities to a great extent. In addition to the transparent SiO_2 the matrix may comprise from 0 to 0.15 mol per mol of SiO_2 of the oxides indicated by MO all of which are transparent to ultraviolet radiation. In this description and the Claims the alkali metals are understood to be the elements Li, Na, K, Rb and Cs and the alkaline earth metals are understood to be the elements Mg, Ca, Sr, and Ba.

In the luminescent quartz glasses according to the invention useful absorption of exciting radiation is effected in the activators Tb and/or Ce. To this end the quartz glass comprises at least 0.75 mol% of Tb_2O_3 and/or Ce_2O_3 with respect to the glass matrix oxides. At lower contents a very low luminous flux is obtained because it has been found that the absorption of the exciting radiation is then too small. The content of the activator oxides is chosen to be equal to at most 15 mol% because at higher values a too low luminous flux is obtained again due to so-called concentration quenching. Quartz glasses with the characteristic green-line emission of Tb^{3+} (maximum at approximately 540 nm) are obtained upon activation by terbium and upon

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activation by cerium an emission of Ce^{3+} is obtained in a band in the blue to near-ultraviolet part of the spectrum. When using both Ce and Tb there is a transfer of excitation energy from the Ce to the Tb.

The addition to the glass matrix mainly comprising SiO_2 of one or more of the transparent oxides of the elements Al, B, P, Zr, Y, La, Gd, Lu, the alkali metals and the alkaline earth metals (up to not more than 0.15 mol per mol of SiO_2) is not necessary to obtain the desired high activator concentration. Such an addition may have the advantage that the glass formation proceeds more easily when preparing the quartz glass and can be effected notably at lower temperatures.

Quartz glasses according to the invention comprising from 1 to 7 mol% of Tb_2O_3 and/or Ce_2O_3 are preferred because the highest luminous fluxes are then obtained.

In a further preferred embodiment of a luminescent quartz glass according to the invention the glass comprises from 0.5 to 5 mol of Al_2O_3 per mol of Tb_2O_3 and/or Ce_2O_3 . In fact it has been found that addition of Al_2O_3 in these quantities is conducive to maintaining or obtaining the desired valency (trivalent) of the activators incorporated in the glass matrix. This particularly applies to cerium.

A very advantageous embodiment of a luminescent quartz glass according to the invention is characterized in that the glass comprises from 0.75 to 15 mol% of Tb_2O_3 and furthermore Eu_2O_3 as an activator oxide in a quantity of not more than 0.2 mol% calculated with respect to the glass matrix oxides. It was surprisingly found that the Tb^{3+} in the luminescent quartz glasses transfers the excitation energy very satisfactorily to Eu^{3+} which then luminesces efficiently. It was found that very small quantities of Eu_2O_3 already yield a contribution of the characteristic red-line emission of Eu^{3+} . When using 0.0005 mol% of Eu_2O_3 the glass still luminesces predominantly green (Tb^{3+} emission) but the red Eu^{3+} emission is already noticeable. With increasing Eu_2O_3 contents the Eu^{3+} emission increases and the Tb^{3+} emission decreases so that luminescent glasses can be obtained with emission colours in the entire range of green to predominantly red. Notably very efficient yellow luminescing quartz glasses are possible which have great advantages for practical uses.

It is to be noted that the use of Eu_2O_3 only as an activator oxide in both high and in low concentrations does not lead to efficiently luminescent glasses because it has been found that upon direct excitation in the Eu^{3+} very low quantum efficiencies are obtained.

Therefore relatively high Tb_2O_3 contents according to the invention are chosen in order to absorb the excitation energy in the Tb and Eu_2O_3 contents which are suitable to obtain the desired emission colour. At a relatively low Eu_2O_3 content of 0.05 mol% this emission colour is already predominantly red. Eu_2O_3 contents of more than 0.2 mol % are not used because then too small quantum efficiencies are obtained due to competitive absorption in Eu^{3+} .

Quartz glasses activated by both Tb^{3+} and Eu^{3+} and comprising not more than 0.01 mol of MO per mol of SiO_2 are preferred because it has been found that the transfer from Tb^{3+} to Eu^{3+} proceeds very efficiently in these glasses.

The best results are obtained with Tb^{3+} and Eu^{3+} activated quartz glasses if the glass comprises from 2 to 7 mol% of Tb_2O_3 and from 0.001 to 0.05 mol% of Eu_2O_3 . Such glasses are therefore preferred.

The luminescent quartz glasses according to the invention can generally be obtained by heating a starting mixture of the composite oxides (with a high degree of purity) or of compounds yielding these oxides upon elevated temperatures in a furnace at a very high temperature until at least the melting point is reached. The melting point is dependent on the composition and, for example, if Al_2O_3 is used in a quantity of 0.02 to 0.10 mol per mol of SiO_2 it is at approximately 2200 °C. During heating of the mixture which is preferably placed in a molybdenum crucible a reducing gas is passed through the furnace to obtain or maintain the Tb and/or Ce in a trivalent state. The melt is maintained at a high temperature some time and is subsequently cooled.

The luminescent quartz glasses activated by terbium or by terbium and europium are preferably prepared by means of a method which according to the invention is characterized in that an alcoholic solution of an alkoxysilane is made to which Tb is added in a quantity of 0.015 to 0.30 mol per mol of Si and to which Eu is added in a quantity of not more than 0.004 mol per mol of Si and furthermore one or more of the elements Al, B, P, Zr, Sc, Y, La, Gd, Lu, the alkali metals and the alkaline earth metals in a quantity corresponding to 0 to 0.15 mol of oxide of these elements per mol of Si are added in the form of an alcoholic solution of at least one compound from the group of alkoxides, nitrates, carbonates and acetates of the said elements, the mixture containing water in such a quantity that gelation occurs, and in that subsequently the gel obtained is dried and the dried gel is heated to a temperature of 500 to 1200 °C.

This method according to the invention uses a technique which is known per se for the formation of glasses having a high SiO_2 content and which is commonly referred to as sol-gel technique. An alcoholic solution of an alkoxysilane is initially used. Very suitable starting materials are tetramethoxysilane and tetraethoxysilane, dissolved in alcohols, preferably the relevant alcohols methanol and ethanol, respectively.

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The desired quantity of Tb and possibly Eu and the desired quantity of the elements which possibly must be incorporated as oxides in addition to SiO_2 in the glass matrix are added to the said solution in the form of an alcoholic solution of alkoxides, nitrates, carbonates and/or acetates of the relevant elements. Furthermore water is added, preferably in a quantity which is sufficient to hydrolyse the silane completely.

5 Due to the hydrolysis a sol is produced which condenses after a certain time so that a gel is formed. The gel obtained is dried and is subsequently heated to a temperature of 500 to 1200 °C so that possibly after pulverisation of the product a glass powder having a very homogenous composition is obtained. When using tetrathoxysilane, for example, a solution is prepared which comprises preferably at least 1 mol of silane per liter of ethanol and to which at least 2 mol of water are added per mol of silane in order to ensure
10 complete hydrolysis. The method according to the invention has great advantages over the method in which the starting mixtures are composite oxides. In fact, a very homogeneous product of a high purity is obtained and the required heating step can be performed at a comparatively low temperature (500-1200 °C).

Such a method according to the invention is preferred which is characterized in that one or more of the alcoholic solutions are brought to a pH value of less than 7 by means of an acid and in that the mixture is
15 brought to a pH value of more than 7 by the addition of a volatile base so that the gelation is accelerated. The use of an acid promotes the required hydrolysis and the use of a base accelerates the subsequent condensation to a gel. If aqueous solutions of an acid and/or a base are used the quantity of water added therewith also counts for the quantity of water required for the hydrolysis.

Due to their high quantum efficiencies the luminescent quartz glasses according to the invention can be
20 used instead of crystalline luminescent materials. Due to their favourable possibilities of processing and shaping the quartz glasses may also be used in luminescent glass fibres. A possible use is also found in cathode ray tubes and in solid-state lasers.

The luminescent quartz glasses according to the invention are preferably used in a luminescent screen which is provided with a luminescent layer comprising the glass and which can be provided on a support.
25 Such screens are used in, for example, discharge lamps such as low-pressure mercury vapour discharge lamps.

The invention will now be described in greater detail with reference to a number of embodiments of luminescent quartz glasses and methods according to the invention and by way of the accompanying drawing.

30 The drawing shows in a graph the spectral energy distribution of the emitted radiation of two quartz glasses according to the invention.

Example 1.

35 An intimate mixture was made of 1 mol of SiO_2 and 0.02 mol of CeAlO_3 . This mixture was heated to 2200 °C in a molybdenum crucible in a high-frequency furnace. The molten mixture was maintained at this temperature for 1 hour. During heating a reducing gas (He with 10% by volume of H_2) was passed through the furnace. Subsequently the melt was cooled. The quartz glass obtained was broken and ground. The
40 pulverulent product (SiO_2 comprising per mol 0.01 mol of Ce_2O_3 and 0.02 mol of Al_2O_3) was found to have a quantum efficiency $q = 43\%$ upon excitation by 254 nm radiation (absorption $A = 76\%$). The emission consisted of a band with a maximum at approximately 410 nm.

Example 2.

45 Starting from a mixture of 1 mol of SiO_2 , 0.01 mol of CeO_2 , 0.03 mol of Tb_2O_3 and 0.07 mol of Al_2O_3 , the same method as described in example 1 was carried out. The glass obtained (SiO_2 with 0.005 mol of Ce_2O_3 , 0.03 mol of Tb_2O_3 and 0.07 mol of Al_2O_3 per mol of SiO_2) had a quantum efficiency $q = 48\%$ upon
50 254 nm excitation ($A = 63\%$). The emission predominantly consisted (> 95%) of the characteristic Tb^{3+} radiation.

Example 3.

55 A solution was made of 1 mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$ in 4 mol of $\text{C}_2\text{H}_5\text{OH}$. 10 mol of water were added to this solution whereafter it was heated at 50 °C for some time. Subsequently a solution of 0.06 mol of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 2 mol of $\text{C}_2\text{H}_5\text{OH}$ was added to the solution while stirring. Due to hydrolysis and condensation

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gelation occurred. The gelation time was found to be approximately two weeks. The gel obtained was dried and then heated in air at 850 °C. After cooling the product was ground so that a fine glass powder consisting of very pure SiO₂ comprising 3 mol% of Tb₂O₃ was obtained. Upon excitation by short-wave ultraviolet radiation (254 nm) the glass was found to have a quantum efficiency of 66%. The absorption A of the
 5 exciting radiation was 81%. The emission consisted of the characteristic Tb³⁺ radiation.

Example 4.

10 The method of example 3 was repeated with the difference that instead of 6 mol of water 108 g of a 0.1 N HCl solution in water (6 mol of water) were added. The gelation took approximately 4 days in this case. The product obtained was substantially equal to that of example 3. A = 80% and q = 96% were measured.

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Example 5.

A solution was made of 1 mol of Si(OC₂H₅)₄ in 4 mol of C₂H₅OH. 36 g of a 0.1 N HCl solution in water (2 mol of water) were added to this solution whereafter it was heated at 50 °C for half an hour while stirring.
 20 A solution of 0.06 mol of Tb(NO₃)₃·5H₂O in 2 mol of C₂H₅OH was added to the clear solution thus obtained. After approximately 10 minutes of stirring 4 mol of a solution of NH₄OH in water (pH = 12) were added whereafter gelation occurred rapidly (gelation substantially complete already after approximately 10 minutes). The gel formed was dried and subsequently heated in air at 850 °C for 1/4 hour. The granular mass obtained was ground for approximately 15 minutes so that a fine glass powder was obtained (very pure
 25 SiO₂ with 3 mol% of Tb₂O₃) which was ready for use. Upon 254 nm excitation (A = 59 %) the powder was found to have a quantum efficiency q of 79%.

Examples 6 to 11.

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Analogously as described in example 5 six luminescent quartz glasses having different compositions were obtained. In these examples, however, the heat treatment was performed for 1/4 hour in air at 900 °C. The following Table states the composition of these glasses as well as the results of the measurements of absorption A of the exciting 254 nm radiation and quantum efficiency q. In the examples 9, 10 and 11 K and
 35 Na, respectively, were added as ethanulates.

Example	Composition	A (%)	q (%)
40 6	1 SiO ₂ ·0.05 Tb ₂ O ₃	63	59
7	1 SiO ₂ ·0.06 Tb ₂ O ₃	34	32
8	1 SiO ₂ ·0.07 Tb ₂ O ₃	65	36
9	0.97 SiO ₂ ·0.03 K ₂ O · 0.03 Tb ₂ O ₃	80	80
45 10	0.92 SiO ₂ ·0.08 Na ₂ O · 0.05 Tb ₂ O ₃	56	72
11	0.85 SiO ₂ ·0.125 Na ₂ O·0.05 Tb ₂ O ₃	68	71

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Examples 12 to 19.

Analogously as described in example 5 eight luminescent quartz glasses were obtained all of which
 55 comprised 5 mol% of Tb₂O₃ and different quantities of Eu₂O₃ in accordance with the formula 1 SiO₂·0.05 Tb₂O₃ x Eu₂O₃. Heating in air was, however, performed at 900 °C. The following Table states for each example the value of the Eu₂O₃ content x as well as the measuring results of absorption A of the exciting 254 nm radiation, the quantum efficiency q and the share of red Eu³⁺ emission (in %).

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Ex.	x	A (%)	q (%)	Eu ³⁺ -em (%)
12	0.000015	69	46	37
13	0.000035	71	58	53
14	0.00005	66	54	69
15	0.00009	70	46	80
16	0.00028	66	49	89
17	0.00054	81	33	91
18	0.00107	70	34	97
19	0.00196	77	23	97

The emission spectrum of the quartz glasses according to examples 13 and 16 is shown in the drawing is a graph in which the wavelength λ is plotted in nm on the horizontal axis. The photon current I is plotted in arbitrary units on the vertical axis. The maximum photon current is set at 100 for both curves. The emission of the glass according to example 13 is yellow to the eye. That of the glass according to example 16 is predominantly red.

Example 20.

A quartz glass defined by the formula $1 \text{ SiO}_2 \cdot 0.075 \text{ Tb}_2\text{O}_3 \cdot 0.0003 \text{ Eu}_2\text{O}_3$ was prepared in a manner as described in example 5. Upon excitation by 254 nm radiation ($A = 85\%$) a quantum efficiency q of 52.5 % was measured. The emitted radiation consisted for 91 % of the red Eu^{3+} emission.

Claims

1. A luminescent quartz glass activated by a rare earth metal, the glass matrix consisting essentially of SiO_2 and furthermore of 0 to 0.15 mol of MO per mol of SiO_2 in which MO represents one or more of the oxides Al_2O_3 , B_2O_3 , P_2O_5 , ZrO_2 , Sc_2O_3 , Y_2O_3 , La_2O_3 , Gd_2O_3 , Lu_2O_3 , ZnO , the alkali metal oxides and the alkaline earth metal oxides, characterized in that the glass comprises at least one of the oxides Tb_2O_3 and Ce_2O_3 as activator oxides in a quantity of 0.75 to 15 mol.% calculated with respect to the glass matrix oxides.
2. A luminescent quartz glass as claimed in Claim 1, characterized in that the glass comprises from 1 to 7 mol% of Tb_2O_3 and/or Ce_2O_3 .
3. A luminescent quartz glass as claimed in Claim 1 or 2, characterized in that the glass comprises from 0.5 to 5 mol of Al_2O_3 per mol of Tb_2O_3 and/or Ce_2O_3 .
4. A luminescent quartz glass as claimed in Claim 1, 2 or 3, characterized in that the glass comprises from 0.75 to 15 mol% of Tb_2O_3 and furthermore Eu_2O_3 as an activator oxide in a quantity of not more than 0.2 mol% calculated with respect to the glass matrix oxides.
5. A luminescent quartz glass as claimed in Claim 4, characterized in that the glass comprises not more than 0.01 mol of MO per mol of SiO_2 .
6. A luminescent quartz glass as claimed in Claim 4 or 5, characterized in that the glass comprises from 2 to 7 mol% of Tb_2O_3 and from 0.001 to 0.05 mol% of Eu_2O_3 .
7. A method of preparing a luminescent quartz glass activated by terbium or by terbium and europium as claimed in any one of the preceding Claims, characterized in that an alcoholic solution of an

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alkoxysilane is made to which Tb is added in a quantity of 0.015 to 0.30 mol per mol of Si and to which Eu is added in a quantity of not more than 0.004 mol per mol of Si and furthermore one or more of the elements Al, B, P, Zr, Sc, Y, La, Gd, Lu, Zn, the alkali metals and the alkaline earth metals in a quantity corresponding to 0 to 0.15 mol of oxide of these elements per mol of Si are added in the form of an alcoholic solution of at least one compound from the group of alkoxides, nitrates, carbonates and acetates of the said elements, the mixture containing water in such a quantity that gelation occurs, and in that subsequently the gel obtained is dried and the dried gel is heated to a temperature of 500 to 1200 °C.

8. A method as claimed in Claim 7, characterized in that one or more of the alcoholic solutions are brought to a pH value of less than 7 by means of an acid and in that the mixture is brought to a pH value of more than 7 by the addition of a volatile base so that the gelation is accelerated.

9. A luminescent screen provided with a luminescent layer comprising a luminescent quartz glass as claimed in any one of Claims 1 to 6, or a luminescent quartz glass obtained by a method as claimed in Claim 7 or 8.

Revendications

1. Verre de quartz luminescent activé par un métal des terres rares, la matrice vitreuse étant essentiellement constituée par SiO_2 et puis 0 à 0,15 mole de MO par mole de SiO_2 , MO représentant au moins l'un des oxydes Al_2O_3 , B_2O_3 , P_2O_5 , ZrO_2 , Sc_2O_3 , Y_2O_3 , La_2O_3 , Gd_2O_3 , Lu_2O_3 , ZnO , les oxydes de métal alcalin et les oxydes de métal alcalino-terreux, caractérisé en ce que le verre contient au moins l'un des oxydes Tb_2O_3 et Ce_2O_3 comme oxyde activant dans une quantité de 0,75 à 15 % en moles calculée par rapport aux oxydes de la matrice vitreuse.
2. Verre de quartz luminescent selon la revendication 1, caractérisé en ce que le verre contient 1 à 7 % en moles de Tb_2O_3 et/ou de Ce_2O_3 .
3. Verre de quartz luminescent selon la revendication 1 ou 2, caractérisé en ce que le verre contient 0,5 à 5 moles de Al_2O_3 par mole de Tb_2O_3 et/ou de Ce_2O_3 .
4. Verre de quartz luminescent selon la revendication 1, 2 ou 3, caractérisé en ce que le verre contient 0,75 à 15 % en moles de Tb_2O_3 et en outre Eu_2O_3 comme oxyde activant dans une quantité d'au maximum 0,2 % en moles calculée par rapport aux oxydes de la matrice vitreuse.
5. Verre de quartz luminescent selon la revendication 4, caractérisé en ce que le verre contient au maximum 0,01 mole de MO par mole de SiO_2 .
6. Verre de quartz luminescent selon la revendication 4 ou 5, caractérisé en ce que le verre contient 2 à 7 % en moles de Tb_2O_3 et 0,001 à 0,05 % en moles de Eu_2O_3 .
7. Procédé pour la préparation d'un verre de quartz luminescent activé à l'aide de terbium ou de terbium et d'euporium selon l'une des revendications précédentes, caractérisé en ce qu'une solution alcoolique d'un alkoxysilane est préparée et additionnée de Tb dans une quantité de 0,015 à 0,30 mole par mole de Si et de Eu dans une quantité d'au maximum 0,004 mole par mole de Si et en outre d'un ou de plusieurs des éléments Al, B, P, Zr, Sc, Y, La, Gd, Lu, Zn les métaux alcalins et les métaux alcalino-terreux dans une quantité correspondant à 0 à 0,15 mole d'oxyde de ces éléments par mole de Si sous forme d'une solution alcoolique d'au moins un composé du groupe d'alkoxydes, nitrates, carbonates et acétates desdits éléments, le mélange contenant de l'eau dans une quantité telle qu'il se produit la gélification et qu'ensuite le gel obtenu est séché et en ce que le gel séché est chauffé à une température de 500 à 1200 °C.
8. Procédé selon la revendication 7, caractérisé en ce qu'une ou plusieurs des solutions alcooliques est (sont) portée(s) à une valeur de pH inférieure à 7 à l'aide d'un acide et en ce que le mélange est porté à une valeur de pH supérieure à 7 par addition d'une base volatile de sorte que la gélification est accélérée.

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9. Ecran luminescent muni d'une couche luminescente contenant un verre de quartz luminescent selon l'une des revendications 1 à 6 ou un verre de quartz luminescent obtenu par un procédé selon la revendication 7 ou 8.

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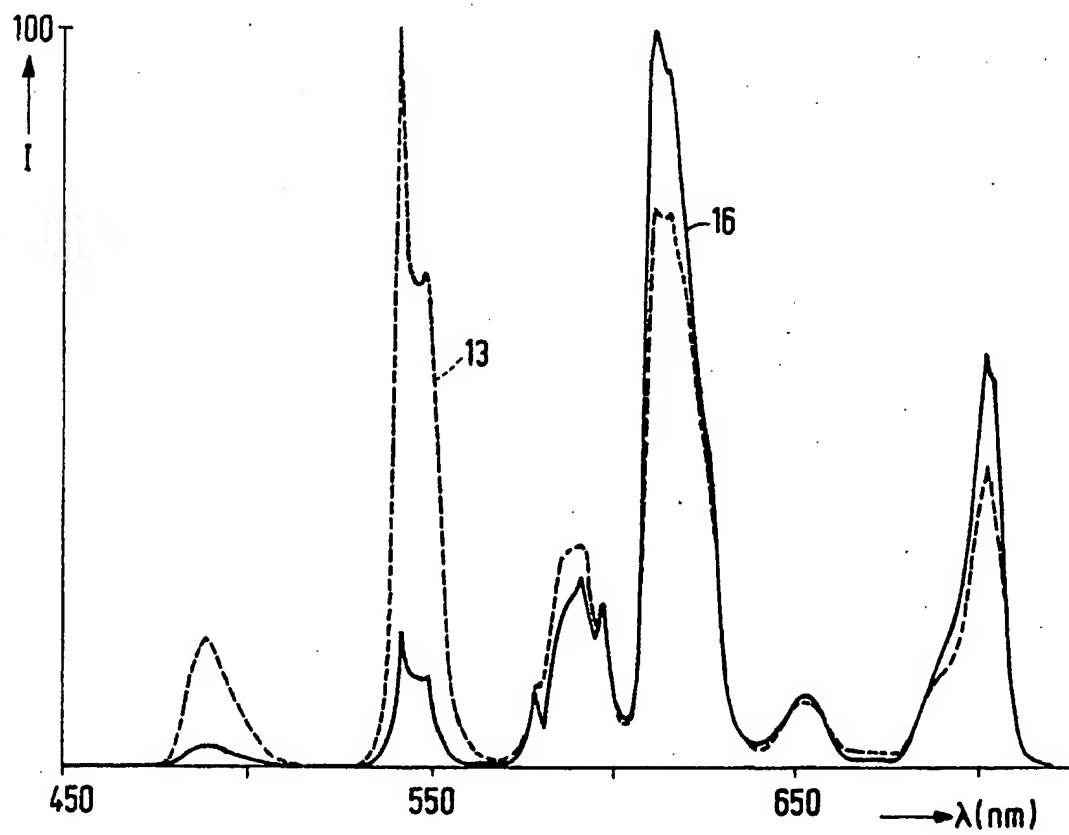
Ansprüche

1. Leuchtendes Quarzglas, das von einem Seltenerdmetall aktiviert wird, wobei die Glasmatrix im wesentlichen aus SiO_2 und außerdem aus 0 bis 0,15 Mol an MO pro Mol an SiO_2 besteht, worin MO eines oder mehrere der Oxyde Al_2O_3 , B_2O_3 , P_2O_5 , ZrO_2 , Sc_2O_3 , Y_2O_3 , La_2O_3 , Gd_2O_3 , Lu_2O_3 , ZnO , die Alkalimetalloxyde und die Erdalkalimetalloxyde darstellt, dadurch gekennzeichnet, daß das Glas wenigstens eines der Oxyde Tb_2O_3 und Ce_2O_3 als Aktivatoroxyde in einer Menge von 0,75 bis zu 15 Mol.% in der Berechnung in bezug auf die Glasmatrixoxyde enthält.
- 10 2. Leuchtendes Quarzglas nach Anspruch 1, dadurch gekennzeichnet, daß das Glas zwischen 1 bis zu 7 Mol.% des Tb_2O_3 und/oder Ce_2O_3 enthält.
3. Leuchtendes Quarzglas nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Glas zwischen 0,5 bis zu 5 Mol des Al_2O_3 pro Mol des Tb_2O_3 und/oder Ce_2O_3 enthält.
- 20 4. Leuchtendes Quarzglas nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Glas zwischen 0,75 bis zu 15 Mol.% des Tb_2O_3 und außerdem Eu_2O_3 als Aktivatoroxyde in einer Menge von nicht mehr als 0,2 Mol.% in der Berechnung in bezug auf die Glasmatrixoxyde enthält.
- 25 5. Leuchtendes Quarzglas nach Anspruch 4, dadurch gekennzeichnet, daß das Glas nicht mehr als 0,01 Mol an MO pro Mol an SiO_2 enthält.
6. Leuchtendes Quarzglas nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß das Glas zwischen 2 bis zu 7 Mol.% des Tb_2O_3 und zwischen 0,001 bis zu 0,05 Mol.% des Eu_2O_3 enthält.
- 30 7. Verfahren zum Zubereiten eines von Terbium oder von Terbium und Europium aktivierten leuchtenden Quarzglas nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, daß eine Alkohollösung aus einem Alkoxysilan bereitet wird, der Tb in einer Menge von 0,015 bis zu 0,30 Mol pro Mol an Si und der Eu in einer Menge von nicht mehr als 0,004 Mol pro Mol an Si zugesetzt werden, und weiterhin eines oder mehrere der Elemente Al, B, P, Zr, Sc, Y, La, Gd, Lu, Zn, die Alkalimetalle und die Erdalkalimetalle in einer Menge entsprechend 0 bis zu 0,15 Mol an Oxyd dieser Elemente pro Mol an Si in Form einer Alkohollösung aus wenigstens einer Verbindung aus der Alkoxydgruppe zugegeben werden, wobei die Mischung Wasser in einer derartigen Menge enthält, daß Gelatinierung auftritt, und daß darauf das gewonnene Gel getrocknet und das getrocknete Gel auf eine Temperatur von 500 bis 1200 °C erhitzt wird.
- 40 8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß eine oder mehrere der Alkohollösungen mittels einer Säure auf einen pH-Wert unter 7 gebracht wird, und daß die Mischung durch Zugabe einer flüchtigen Base auf einen pH-Wert über 7 gebracht wird, so daß sich die Gelatinierung beschleunigt.
- 45 9. Leuchtschirm mit einer Leuchtstoffschicht mit einem leuchtenden Quarzglas nach einem der Ansprüche 1 bis 6, oder mit einem leuchtenden Quarzglas, das mit dem Verfahren nach Anspruch 7 oder 8 erhalten wird.

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